

Metal-Induced Crystallization

My research at the Helmholtz Zentrum is focused on an effect termed metal-induced crystallization. This describes the assisted crystallization of semiconductor thin-films through the introduction of a blanketing layer of metal (in our case aluminum). The metal in this case acts as a doping agent, and has the effect of lowering the crystallization temperature of the blanketed semiconductor layer. This defines a so-called eutectic mixture—one in which the crystallization temperature of the system is lower than either of its constituent parts. This exciting phenomenon allows for the use of low-cost or temperature-sensitive materials in the production of polycrystalline silicone, a material that is ubiquitous in the electronics industry and can be found in solar panels, compact electronics, and electronic displays. Metal induced crystallization is most useful as an effect because it lowers the crystallization temperature of the silicon substrate. A lower crystallization temperature in production, besides the obvious energy savings, would allow for the use of temperature-sensitive substrates in the production of the aforementioned devices. Flexible materials such as Forex would enable the production of similarly flexible solar panels, which could be used to cover the chassis of cars while preserving their aerodynamic properties. Additionally, the usage of aluminum as a dopant does away with the need to further dope the silicon¹.

A process called sputter deposition is used to deposit the aluminum film in tens-of-atoms thick uniform layers. Sputter deposition was pioneered as a manufacturing technique in the semiconductor industry, and continues to be one of the most efficient and reliable means of producing thin films with a high degree of homogeneity. The sputtering process begins with the placement of a substrate into an ultra-high vacuum² chamber. The chamber must be evacuated of all impurities to ensure homogeneity of the deposited layer. The chamber is then filled with highly-energized plasma composed of ionized argon gas. The argon ions bombard a “target”, which is a composed of the material that one intends to deposit. Atoms ejected from the target form a uniform

¹the process of “doping” broadens the bandgap between a p-type and an n-type semiconductor, which increases the electrical efficiency of a solar cell.

²Ultra-high vacua (UHV) are defined as being at a pressure lower than 10^{-9} mbar.

cloud in the deposition chamber, some of which land on the substrate, forming a thin film on its surface. The thickness and uniformity of the film can be controlled by varying the sputter rate, which is in turn determined by the sputter power³ and the distance between the substrate and target. Figure 1 shows a plot of sputter rate vs. power, and figure 2 shows us how sputter rate varies with distance. As we can see, sputter rate varies linearly with power, as an incremental change in the energy of the bombarding plasma will correspond to an incremental change in the ejection of atoms from the sputter target. The relationship between sputter rate and target-substrate distance follows a more complicated function. This is because, as we move farther away from the source, the density of the ejected atoms decreases by a factor of the square of the distance⁴.

In our experiment, three Corning glass inch-by-inch samples were placed into our ultra-high vacuum “SISSY” system to be sputtered. The sputter power was varied, as a layer of aluminum was sputtered onto each sample for one minute. The sputter powers used were 30, 60, and 90 Watts for samples one, two, and three, respectively. By measuring the layer thicknesses in the adjacent EMIL Lab with a profilometer, we were able to compute how layer thickness varied with sputter power (the sputter rate). This allowed us to properly calibrate the experimental setup, to a degree at which we could reasonably estimate layer thickness based on sputter power and time. This knowledge made it possible to gauge layer thickness without exposing our samples to air by withdrawing them from the sputter chamber. Exposure to air would oxidize the deposited aluminum layer, forming a film of aluminum oxide on its surface.

After profiling our aluminum-deposited samples, we placed them back into the sputtering chamber at SISSY, and sputter them with a layer of Silicon. The samples were then re-probed for thickness. Immediately after sputtering, and without

³Which corresponds to the energy of the plasma ions.

⁴This is an example of the so-called inverse-square law, in which moving away from some point source in three-dimensional space will yield a rapidly decaying “influence” on an observer. Gravity, for example, follows an inverse square law, as we can approximate spherical masses as point-sources. If at 100km away from the Earth, I feel a force F , at a distance of 200km, I will feel a force $\frac{F}{4}$

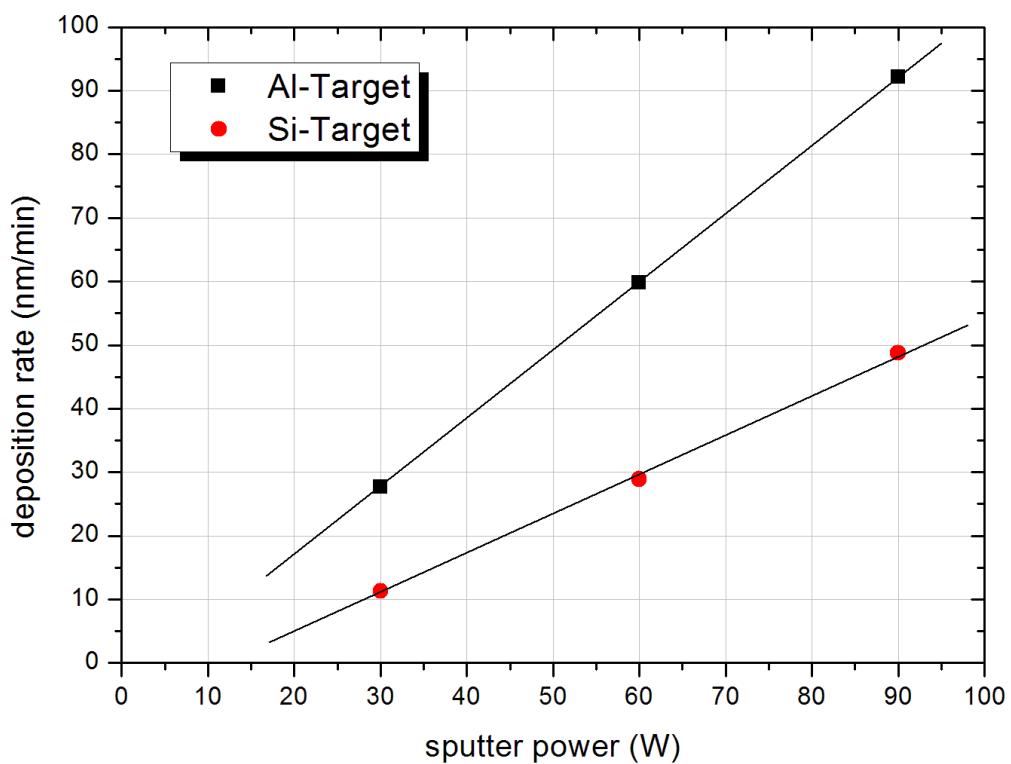


Figure 1: The influence that power has on sputter rate

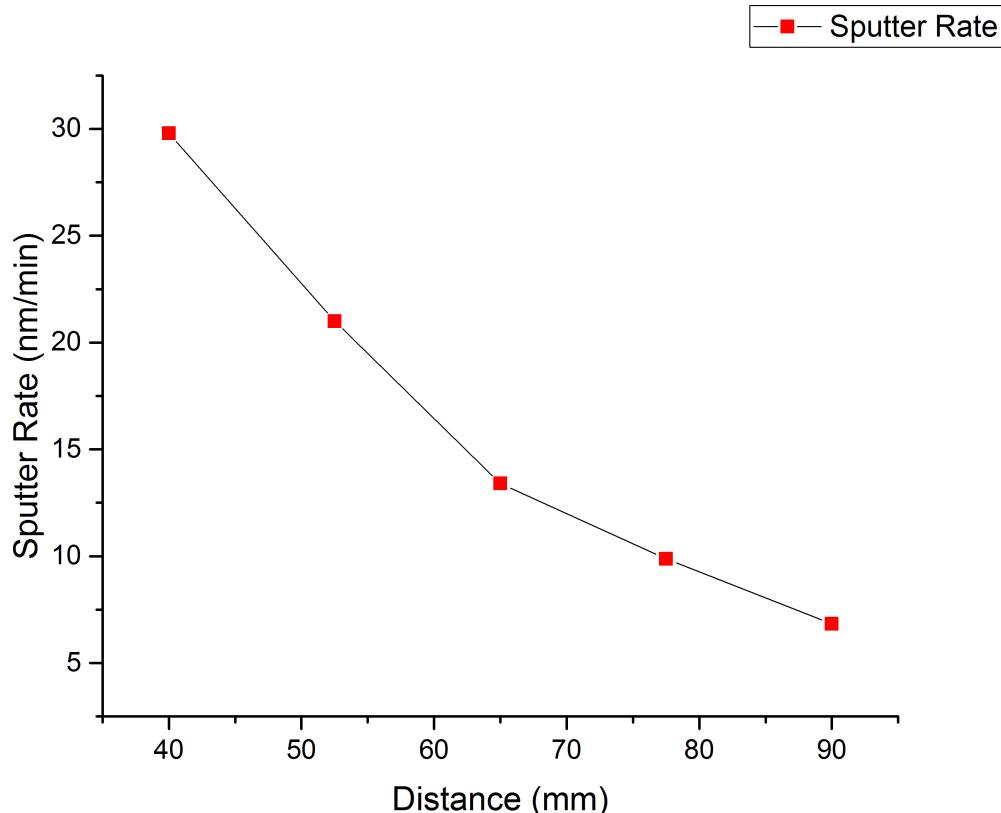


Figure 2: Sputter rate versus sputter distance

leaving their ultra-high vacuum environment, the samples were brought into an analytic chamber via external manipulator. The samples were then analyzed using X-ray photoelectron spectroscopy.

X-ray photoelectron spectroscopy is an analytic technique which allows us to determine the composition of materials. Einstein's discovery of the photoelectric effect (for which he won a Nobel Prize in 1921⁵) is the guiding principle behind the technique. In XPS, coherent light⁶ at discrete energies is directed at the material in question which, in turn, ejects electrons with energies proportional to that of the incident light. It is with the emergence of quantum theory that we came to realize that atomic energies are quantized, and therefore useful in identifying elements. The number of electrons present in an atom largely determines its behavior, and—assuming non-ionized atoms⁷—are enough to uniquely identify a material. A given atom might

⁵16 years after he published its discovery...

⁶In which all photons are of equal wavelength and phase.

⁷i.e., those which are electrically neutral.

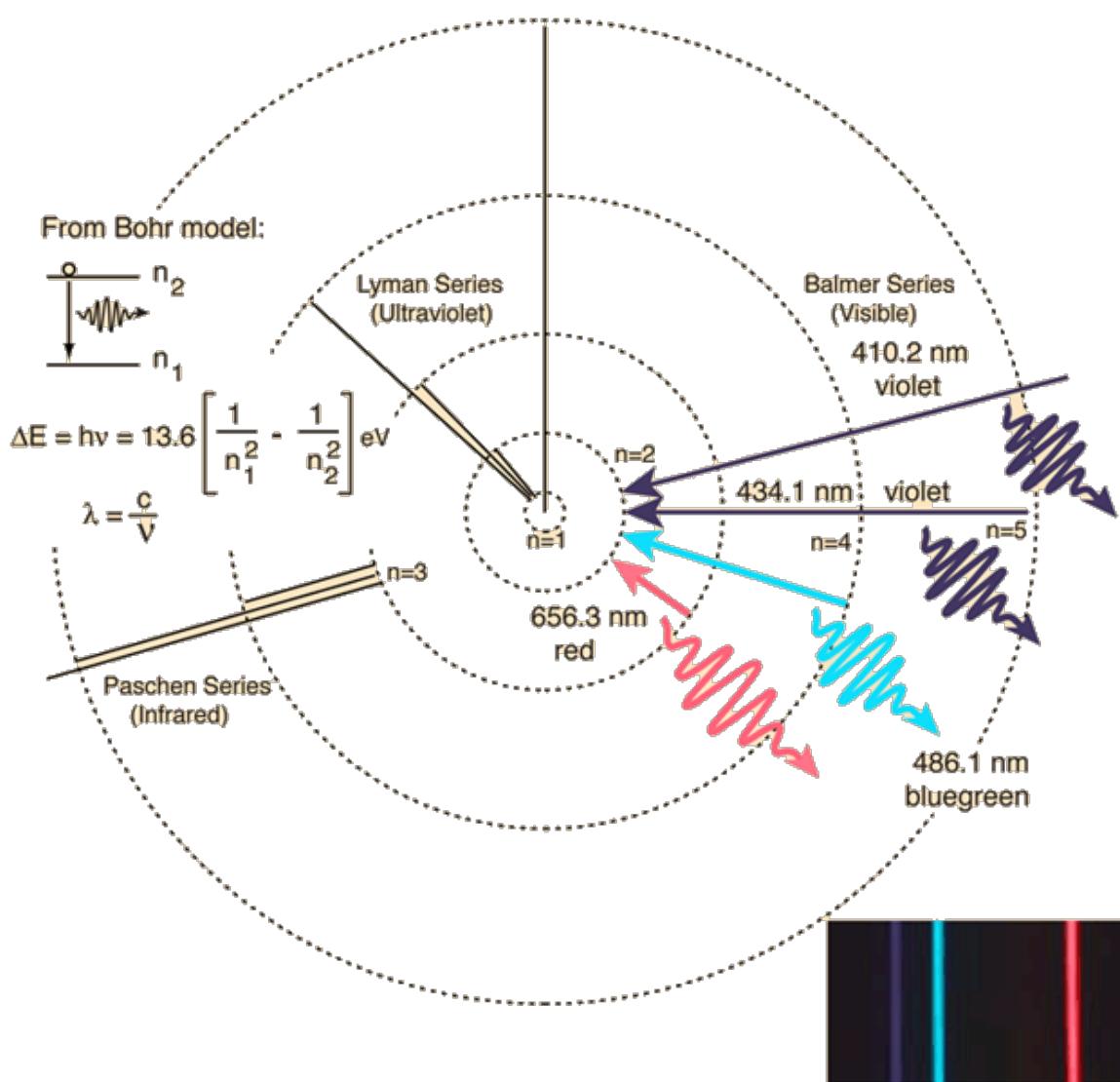


Figure 3: The quantized energy levels in a hydrogen atom.

contain several electrons, occupying so-called orbitals at discrete energies. A hydrogen atom, for example, contains one electron, at an energy of 13.6eV in the ground-state. This energy corresponds to the ionization energy of the atom⁸.

Ramping up through the energies 1200 to 0 eV⁹, we were able to wholly determine the elemental makeup of the surface of our samples. As expected, the dominant element in these samples was silicon, because this was the last material that we sputtered. The samples also contained trace amounts of argon, which likely came from the plasma that

⁸This is to say that you would need 24.6eV of energy to ionize Helium into its constituent parts, a proton and an electron

⁹The electron volt is a unit of energy defined as the amount of energy gained by the charge of a single electron moved across an electric potential difference of one volt. The energies are “ramped up” from 1200 to 0 eV, because electrons are negatively charged, and therefore 1200eV, as far as XPS is concerned, is less than 0eV.

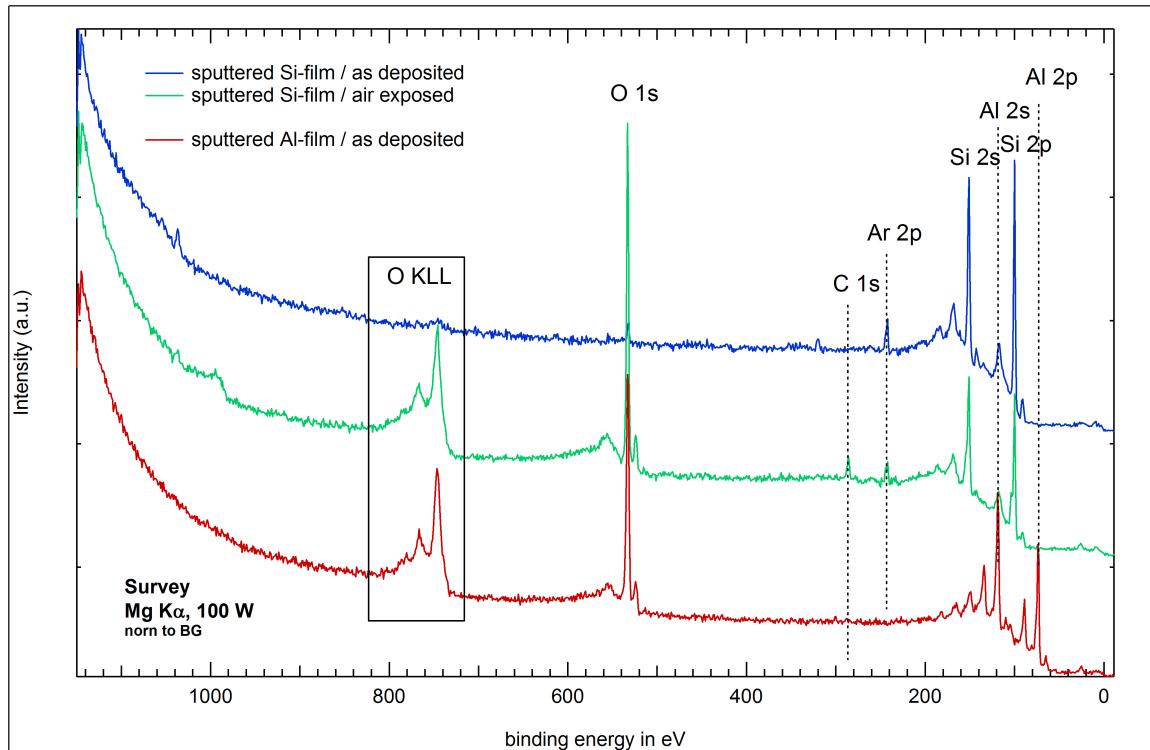


Figure 4: Characteristic spectra from our initial XPS measurements. An aluminum-sputtered sample was analyzed for completeness.

we used to bombard the target; and oxygen, a common contaminant¹⁰. The spectra from our XPS measurements can be found in figure 4.

After taking our preliminary XPS measurements, we brought our samples to a laboratory in Wannsee for annealing. As previously mentioned, in order for the metal-induced crystallization process to occur, samples must reach some critical eutectic temperature. This allows the constituent atoms in each deposited film to move freely, initiating a layer exchange process. It is through this layer exchange that the amorphous silicon becomes crystallized. The samples were annealed in a glovebox at a temperature of roughly 300C, a figure we got from an earlier publication on the topic. One sample was annealed in argon gas, and the other in air. The samples were then brought to another lab in the Helmholtz Zentrum Wannsee campus to be given the XRD-treatment.

X-ray diffraction, or XRD, is a technique by which we can determine the structure

¹⁰Oxygen is extremely reactive, and therefore bonds easily to non-inert materials in the sputter chamber.

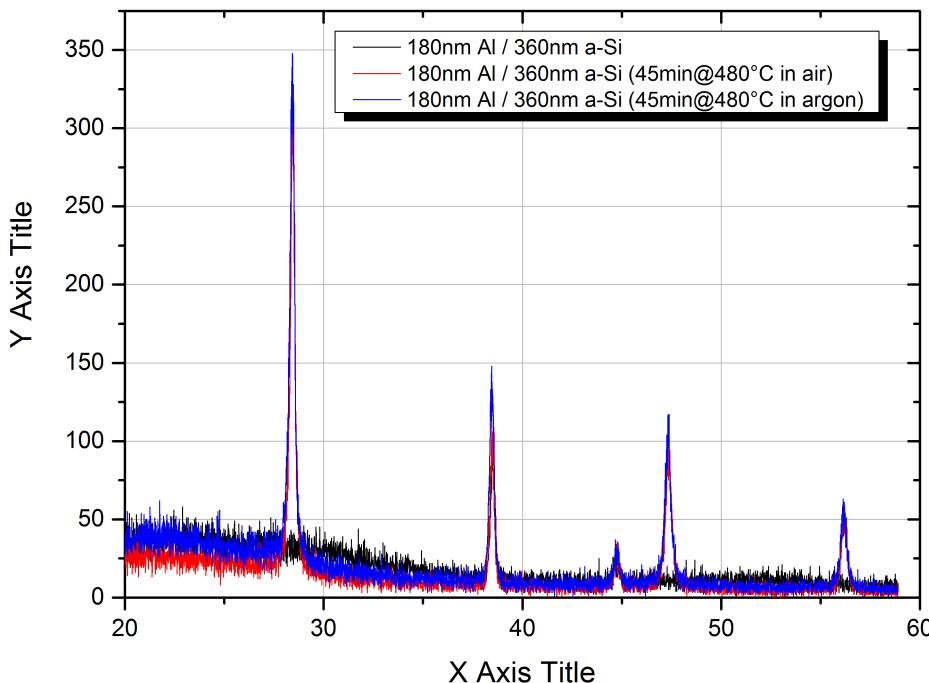


Figure 5: XRD spectra for the air-annealed, argon-annealed, and un-annealed samples

of crystalline lattices¹¹. By rotating a platform on which a sample is placed, we can determine the lattice constant (which refers to the mean distance between atoms in the structure) through analyzing the angles at which constructive interference in the incident light occurs. Like x-ray photoelectron spectroscopy, x-ray diffraction provides us with a spectrum along which peaks can be seen at discrete intervals, allowing us to better characterize a material in question. Figure 5 shows us the angles at which the most constructive interference can be found. Comparing the spectrum of the unannealed sample (again, included for completeness) to the spectra of the two annealed samples (which we find to be identical), we can clearly see the growth of three additional spectra. These spectra are evidence of silicon crystal growths and correspond to crystal structures oriented in the (1,1,1), (1,0,0), and (1,1,0) directions from left to right (see figure 6). The background peaks (shown in black) come from the aluminum thin film, which is also crystalline.

After annealing the samples, we returned to our lab in Aldershof and took ad-

¹¹It is for this reason that we brought the samples to the XRD lab after they had been crystallized.

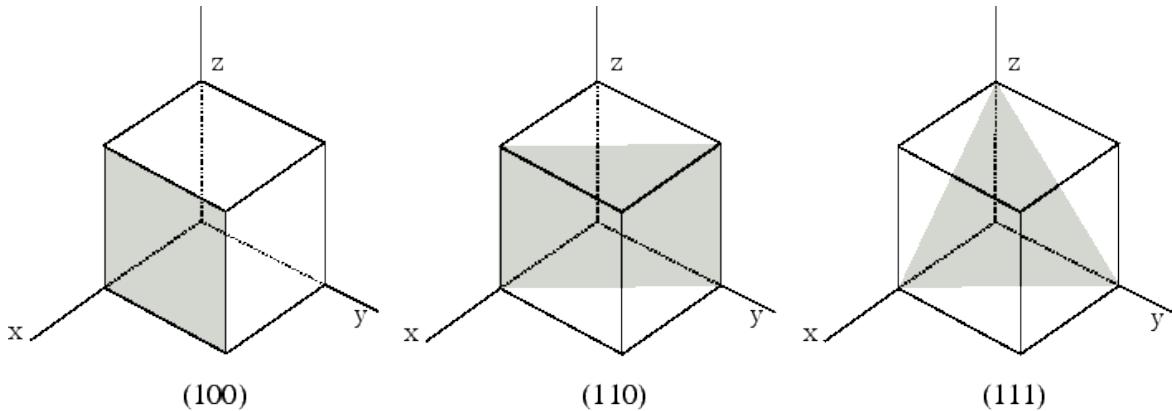


Figure 6: The orientations of our silicon crystal growths

ditional XPS measurements. Seen in figure 8, these spectra show clear evidence of the layer exchange process. Because the energy of the light from our photon source is typically not high enough to penetrate more than a few layers of our sample, the composition that we see from XPS is only of the materials surface. In this case, this works to our advantage, because a decrease in the level of silicon, and the appearance of aluminum in our sample will indicate that layer exchange has occurred. We found that, after annealing, the argon gas on the samples' surface had vanished. We suspect that, during the sputtering process, microcavities of argon gas (the inert gas used to bombard our silicon target) were formed. In the layer-exchange process, these cavities were re-opened, allowing the argon gas to escape. This initial gas-trapping effect could be mitigated with a lower sputter power, which would consequently reduce the kinetic energy of the argon ions, giving providing them with less energy to sink into the deposited silicon film. A lower sputter power would also provide us with a more homogenous silicon surface, which is understood to aid in the formation of larger crystalline growths. With a lower sputter power, however, comes a lower sputter rate, which is undesirable in industrial applications. Figure ?? shows the relative concentration of argon in our sample before and after the annealing process.

Following our second series of XPS measuring, we decided to take a closer look at the samples that we had been toiling over. Scanning electron microscopy, or SEM, can be helpful in obtaining an idea of the local topography of the surfaces of materials. In this technique, single electrons are shot at a material's surface in sequence, and their absorption spectra are used to resolve an image of it in very high detail. SEM

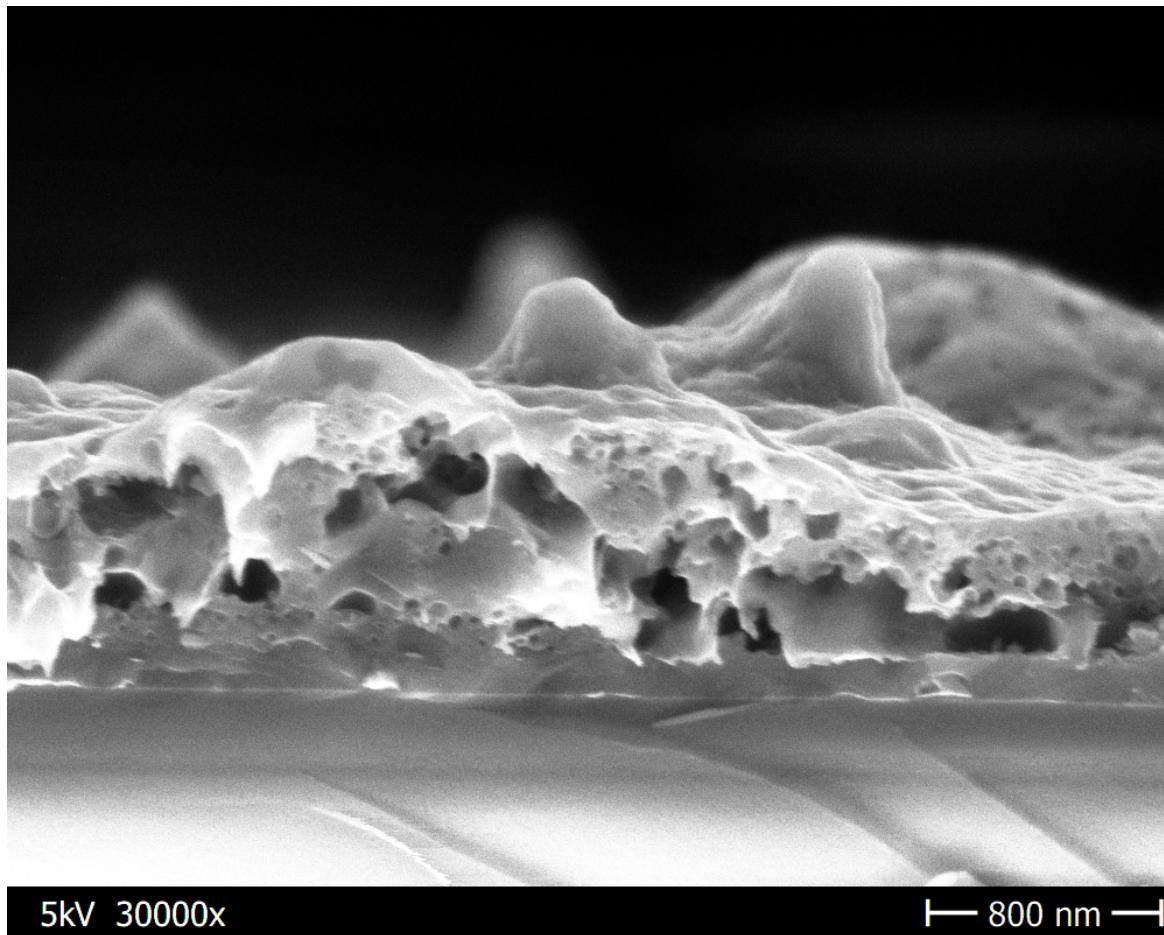


Figure 7: An SEM image of one of our annealed samples with aluminum foam

must be done in an ultra-high vacuum setup to reduce noise in the image. We cut the annealed samples into pieces small enough to fit into the microscopy chamber, and positioned them at a 30 degree angle relative to the electron source. This allowed us to get a view of the silicon-aluminum wafers in cross-section, which can be seen in figure . We discovered a layer of material on the surface of our samples which we initially suspected to be “aluminum foam”. Literature on the topic had told us that this could be etched off by immersing the sample in a bath of hydrochloric acid (HCl) for a short period. This however was not the case for us, and we saw no change in SEM or XPS results after HCl immersion. We tried again with a higher concentration of HCl¹², but got the same results. This leads us to believe that the “foam” seen on top of our samples may not be what we think it is, but we have yet to investigate this further.

¹²Hydrochloric acid is unstable at standard temperature and pressure, and must be suspended in an aqueous solution. The highest concentration available is 37.0% HCl in 63.0% water.

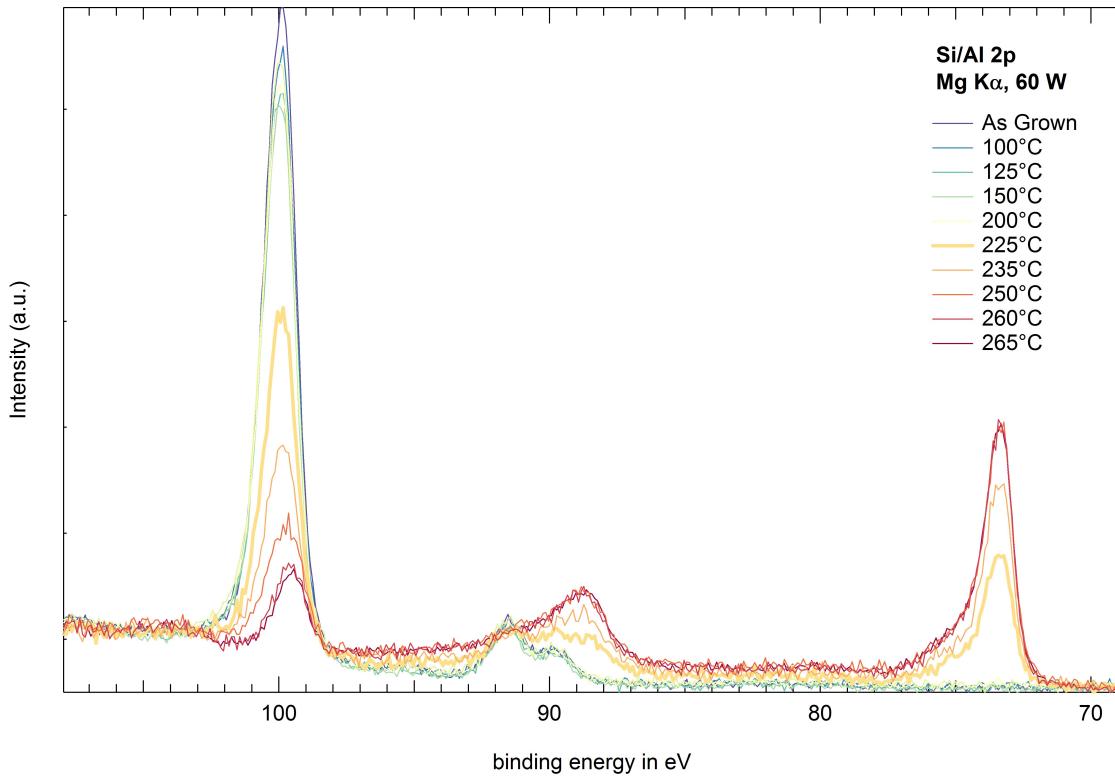


Figure 8: In-situ XPS spectrum of the layer exchange process

Through the course of our experimenting, we began to notice a dependence on thickness in the minimum crystallization temperatures of our samples. To test this theory, we fabricated a very thin wafer using 20 nanometers of silicon atop 40 nanometers of aluminum¹³. We then moved this sample to the analytic chamber of the SISSY system and crystallized it using a ramp-up anneal to 280C using a heatable sample holder. By annealing to a lower temperature in the analytic chamber, we were able to take XPS measurements “in-situ” as the sample was crystallized. Figure 8 shows a segment of the XPS spectrum as the sample is heated over time. Here we are able to see the mechanics of the layer exchange: the process starts with a diminishing of silicon intensity, which suddenly disappears and is replaced by a rapid increase in the aluminum peak. After a period, the aluminum growth levels off, indicating that the sample is fully crystalline. Figure 9 shows a three-dimensional plot of the same experiment, using a sample with slightly greater layer thickness (60nm Al/40nm Si) than the previous.

¹³to give you an idea of how thin this is, the thickness of an average human hair is about 200 times this.

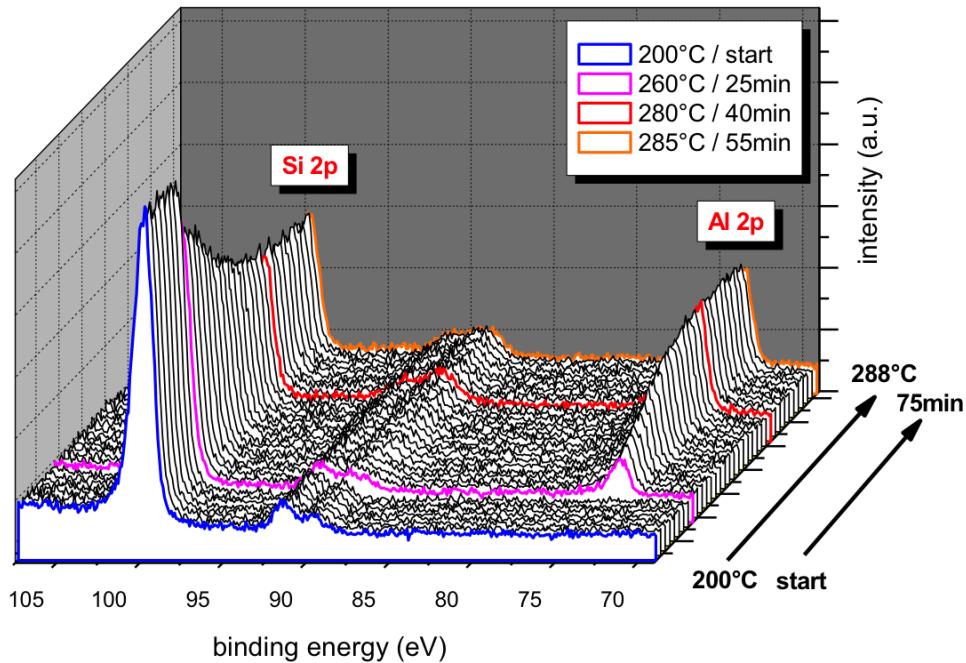


Figure 9: 3D XPS plot of the annealing process

This new in-situ XPS measurement technique will allow us to construct a model of how crystallization temperature varies with layer thickness, giving us the ability to fine-tune the material properties of our deposited structures. Our hope is to quickly bring this knowledge to industry, where it will be used in energy materials like thermoelectric and photovoltaics. Crystalline silicon is a semiconductor, which means that it experiences the photoelectric effect discussed above. My hope is that this new process will be used in the development of flexible solar panels and thermoelectric generators. A sheet of flexible solar panel could be used to “wrap” an electric car, maximizing the area of energy conversion while retaining the aerodynamic properties of the car’s exterior. Flexible thermoelectrics, which operate like solar panels but in the infrared range (heat), could be used to create baffles around heat-emitting machine components, like combustion engines. This would re-capture the waste heat emitted by the engine and increase its efficiency by up to 14%! Whatever the outcome of my research, it will feel great to have contributed to a cleaner energy future.